



Dearborn Environmental Consulting Group
Dearborn Chemical Company Limited
Subsidiary of VWR, Grace & Co

3451 Erindale Station Rd.
P.O. Box 3060, Station A
Mississauga, Ontario, Canada L5A 3T5
Telephone: (416) 279-2222
Telex: 06-961145
Fax: (416) 279-0020

CONTRACT REPORT NO. 89242-01-SQ

CONTRACT REQUISITION NO. 23440-8-9242

CONTRACTOR: DEARBORN ENVIRONMENTAL
CONSULTING GROUP

CHEMICAL AND GEOTECHNICAL TESTING OF COMBUSTION
SOLID WASTES FOR THEIR COMMERCIAL APPLICATION

FOR

CANMET
ENERGY MINES AND RESOURCES CANADA

MICROMEDIA

PREPARED BY
DEARBORN ENVIRONMENTAL CONSULTING GROUP
AUGUST 7, 1989

TABLE OF CONTENTS

	Page
LIST OF FIGURES	iii
LIST OF TABLES	iv
1 INTRODUCTION	1
1.1 Objectives	2
1.2 Source of Residues	2
2 GEOTECHNICAL CHARACTERIZATION	6
3 CHEMICAL CHARACTERIZATION	14
4 SULPHUR SPECIATION	19
4.1 Chemical Characteristics	21
4.2 Phase Composition	26
4.3 Sulphur Speciation and the Mechanisms of Formation of CaS	26
4.4 Summary	30
5 DISCUSSION	32
6 REFERENCES	36

LIST OF FIGURES

Figure		Page
1	SOURCE OF SAMPLES	4
2	GRAIN SIZE DISTRIBUTION FROM SIEVE ANALYSIS ONLY	7
3	GRAIN SIZE DISTRIBUTION USING SIEVE AND HYDROMETER ANALYSIS	8
4	STANDARD PROCTOR COMPACTION CURVE	10
5	X-RAY DIFFRACTION PATTERNS (CuK) FOR SAMPLE C2-7 RECOVERED FROM THE CFB COMBUSTOR SHOWING IDENTIFICATION OF PHASES: Q, QUARTZ, H, HEMATITE, MAG, MAGNETITE, A, ANHYDRITE, CaO, CALCIUM OXIDE.	20
6	THERMOGRAVIMETRIC ANALYSIS CURVES FROM CFBC RESIDUES SHOWING MASS LOSS ABOVE 750°C.	24
7	DETAILS OF THE XRD PATTERNS FOR SAMPLES C1-1, C1-7 AND C2-7 IN THE 2.00 Å REGION SHOWING THE OVERLAP OF DIFFRACTION LINES DUE TO ANHYDRITE (Å) AND CALCIUM SULPHIDE (CaS).	25
8	COMPARISON OF PARTICLE SIZE DISTRIBUTION	33

LIST OF TABLES

Table		Page
1	SCHEDULE OF COMBUSTION TRIALS AT UBC PILOT PLANT	3
2	CHEMICAL ANALYSES OF CFBC RAW MATERIAL	5
3	SUMMARY OF UNCONFINED COMPRESSIVE STRENGTH TESTING OF LABORATORY COMPACTED SAMPLES ON BLENDED MATERIAL	12
4	SUMMARY OF CONSTANT HEAD HYDRAULIC CONDUCTIVITY TESTING OF LABORATORY COMPACTED SAMPLES ON BLENDED MATERIAL	13
5	SUMMARY OF ANALYTICAL METHODS	14
6	ANALYSIS BY X-RAY FLUORESCENCE - MAIN COMPONENTS	15
7	TRACE COMPONENTS	15
8	ANALYSIS OF TOTAL SULPHUR, SOLUABLE SULPHATES AND SULPHIDES BY WET CHEMISTRY	15
9	ANALYSIS OF CARBON DIOXIDE AND TOTAL CARBON	16
10	RESULTS OF XRD ANALYSIS	17
11	TITRATION OF CaO	17
12	ESTIMATED COMPOSITION OF THE SAMPLES IN TERMS OF CHEMICAL COMPOUNDS	18
13	CHEMICAL ANALYSIS (MASS %) OF FBC RESIDUES (C2-SERIES)	22
14	CHEMICAL ANALYSIS (MASS %) OF FBC RESIDUES (C1-SERIES)	22
15	THERMOGRAVIMETRIC MASS LOSS (%) FROM FBC RESIDUES (C2-SERIES)	23
16	CALCULATED PHASE COMPOSITION OF FBC RESIDUES (C2-SERIES)	27
17	CALCULATED PHASE COMPOSITION OF FBC RESIDUES (C1-SERIES)	27
18	COMPARISON OF GEOTECHNICAL PROPERTIES	34
19	COMPARISON OF CHEMICAL COMPOSITION	35

1 INTRODUCTION

The geotechnical properties and formation of sulphides in solid residues from Circulating Fluidized Bed Combustion (CFBC) units are not well understood. It also appears that compared to full-scale combustors, residues from pilot-scale equipment have less desirable geotechnical properties for waste disposal and can contain high quantities of sulphides.

In a recent study conducted at the University of British Columbia (UBC), wastes were generated during a combustion trial with Minto coal and a mixture of Elmtree and Texlime limestones as a sulphur sorbent. This work was done under contract to EMR and was part of a program to compare the geotechnical properties and sulphide formation in wastes produced by pilot-scale units with those from the full-scale, 22 MW_e CFBC Boiler, at Chatham, New Brunswick. The aim of this work was to develop correlations that could be used to predict the properties of the waste solids from the Chatham CFBC unit and in the long term properties of waste residues from any full-scale CFBC unit.

The results of the subsequent analysis indicated that residues from the pilot-scale unit had much less desirable geotechnical properties for both waste disposal and utilization than those from the Chatham unit. In addition the baghouse streams had up to an order of magnitude more CaS, which means that residues from the pilot-scale unit may require special handling and disposal considerations. The pilot-scale residues therefore were not representative, of the Chatham unit even though a similar fuel/sorbent combination was used, and the operating conditions were kept as similar as possible to those of the Chatham unit.

The development of suitable correlations for waste properties between pilot and full-scale combustors is of major importance since in most cases it is not feasible to generate residues from full-scale units, at will, for the purposes of geotechnical testing. The high concentrations of sulphide present in residues from the pilot-scale unit is also of concern. Pilot-scale units appear to give misleading information about the environmental hazards associated with solid residues from the CFBC systems. This could adversely effect the marketing of the technology and result in unduly complex and expensive waste management practices.

Subsequently the UBC pilot-scale unit was modified to improve the combustion performance. Modifications included adding a V-valve to the secondary cyclone and altering the combustor bottom in order to achieve better combustor performance. A second set of samples was generated during an extended duration combustion trial with Minto coal and Havelock limestone which had considerably better combustion efficiency and sulphur capture. The effects of changing limestone may also effect these properties. It is expected that these residues should be more typical of those obtained from good CFBC operation.

1.1 Objectives

The overall objectives of this investigation was to characterize residues produced at the modified UBC pilot-scale combustor in order to permit comparison with the results of previous testing. To achieve this, the same analytical techniques had to be used. A second objective was the analysis of samples from the combustion loop for reduced sulphur forms. These samples were obtained, stored and analyzed under nitrogen to prevent their deterioration.

1.2 Source of Samples

Samples which were characterized during this study were generated by the combustion of Minto coal in a bed of Havelock limestone during the period of December 9-11, 1988. The proportions of solid wastes produced were as follows:

Baghouse catch	50.5%	(position 7)
Secondary return	39.3%	(position 6)
Bed and "L"-valve drain	10.2%	(position 1 & 5)

All samples were taken after steady-state conditions had been achieved; ie: from 5:00, December 10, 1988 until the end of test run 2 at 15:00, December 10, 1988. Table 1 presents the complete schedule of combustion trials on the UBC pilot-plant during which the samples were generated. Figure 1 identifies the sampling locations around the combustion loop. Table 2 presents the results of analyses of the raw materials used during the test program.

TABLE 1 SCHEDULE OF COMBUSTION TRIALS AT UBC PILOT PLANT
RUN SCHEDULE

<u>Date</u>	<u>Time</u>	<u>Activity</u>
Friday 9/12/88	9:00	Start-up
	10:15	Highvale coal feeding
	12:35	Minto coal feeding
	14:00	Minto/Havelock Ca/S=3.01 feeding
		A period of 15 hours is needed to reach solids composition steady-state in the system. Conditions are for test run 1.
Saturday 10/12/88	5:00	Solids samples A collected.
	6:00	Start of condition test run 1.
	10:00	Start of condition test run 2.
	15:00	Solids samples B collected.
	15:30	Switch to Minto/Havelock Ca/S=1.81
	18:00	Start of condition test run 3.
Sunday 11/12/88	22:00	Start of condition test run 4.
	1:00	Reduce load to condition test run 4'.
	2:30	Solids samples C collected.
	8:45	Switch to Minto/Havelock Ca/S=3.01
	10:45	Stop secondary cyclone fines recycle, start of condition test run 5.
	14:00	Solids samples D collected.
	14:30	Run terminated.

TEST RUNS

<u>Conditions</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>4'</u>	<u>5</u>
Primary air (SCFM)	49	33	33	49	42	42
Secondary Air (SCFM)	47	63	63	47	45	45
S/P air ratio (-)	0.96	1.91	1.91	0.96	1.07	1.07
Superficial Velocity (m/s)	8.3	8.3	8.3	8.4	7.5	7.6
Temperature (°C)	882	890	891	900	878	895
Ca/S ratio (mol/mol)	3.01	3.01	1.81	1.81	1.81	3.01

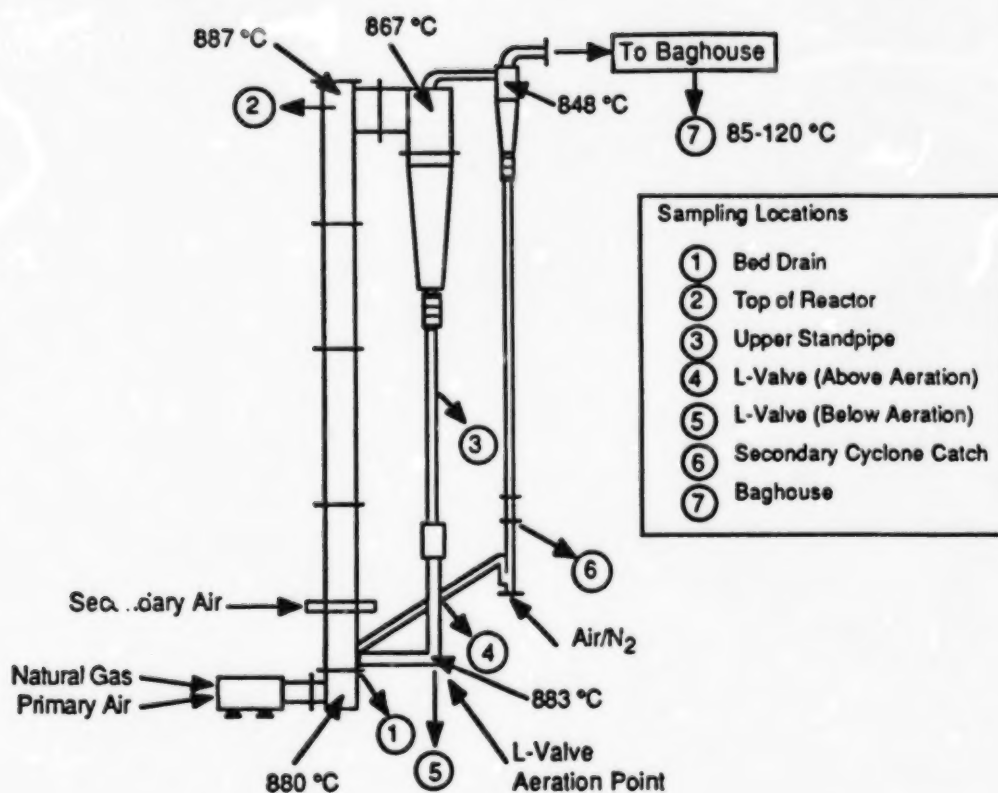


FIGURE 1 SOURCE OF SAMPLES (1)

TABLE 2 - CHEMICAL ANALYSES OF CFBC RAW MATERIALS

Element Oxide	Olivine Sand	Texlime	Havelock	Minto Coal Ash
SiO ₂	41.48	0.00	1.30	39.32
Al ₂ O ₃	0.76	0.62	0.20	12.52
Fe ₂ O ₃	8.58	0.45	0.20	39.8
CaO	0.14	54.57	55.0	2.64
MgO	48.08	0.34	0.20	0.43
Na ₂ O	0.05	0.05	0.03	0.2
K ₂ O	0.01	0.16	0.20	1.58
SO ₃	0.54	1.17	N.A.	2.09

The fuel used during this combustion test was a Minto coal from New Brunswick. As is the case with all pilot-scale CFBC units it was necessary to employ a "start-up" bed, heated by propane gas, to raise the temperature of the system prior to addition of limestone and coal. During this combustion run, a coarse olivine sand was used. The limestone used was from Havelock, N.B. Chemical analyses of the olivine sand, coal ash and limestones were provided by Dr. J. Grace of UBC.

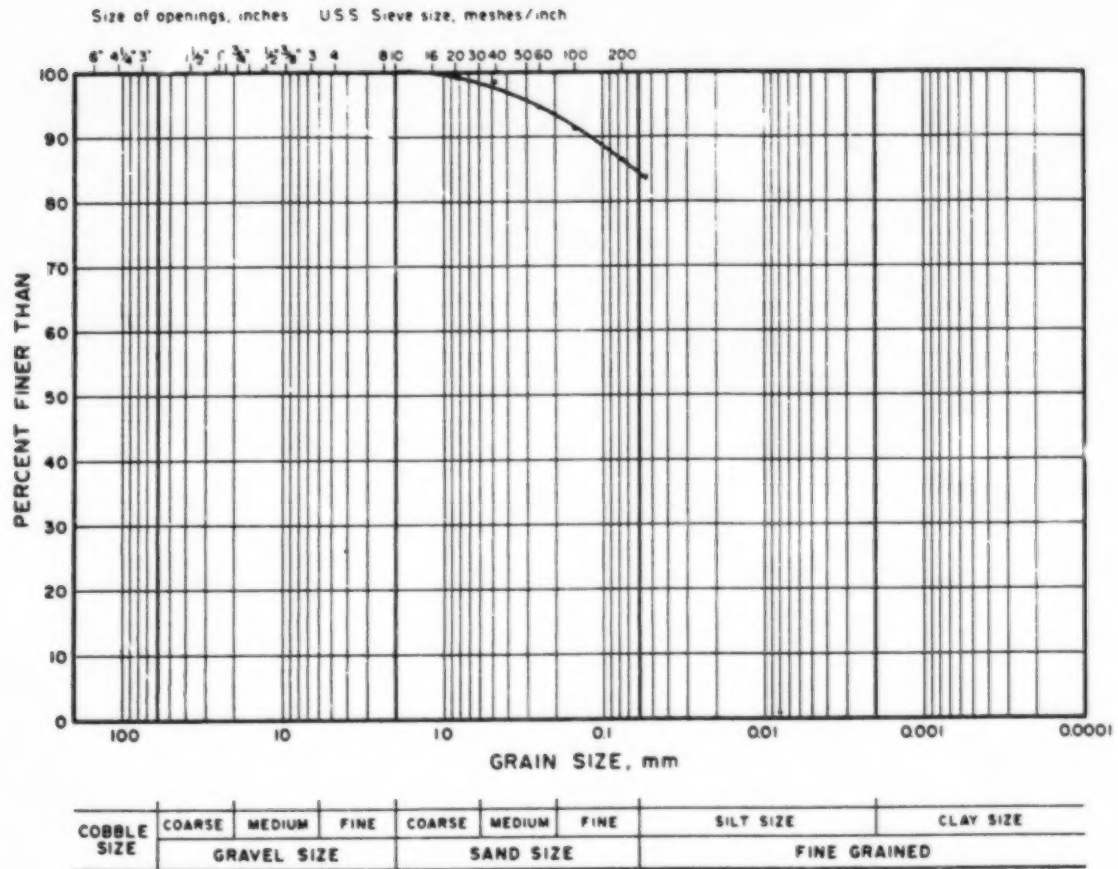
All geotechnical characterizations were carried out on a blended sample with the proportions of 50.5% baghouse capture, 39.3% secondary cyclone return and 10.2% bed drain. Five tests were performed on this sample. The purpose of each test and the results achieved are presented below.

Particle Size Analysis The particle size distribution was determined following ASTM method D 422-63(2). The quantitative distribution of particle size was made by sieving particles with sizes larger than 52 μm (retained on No. 270 sieve). These results are presented on Figure 2. A hydrometer (using water) was used to determine the distribution of particles smaller than 75 μm . The combined results from the sieving and hydrometer are given on Figure 3.

The particle size distribution or gradation provides a means of describing a soil type, e.g. silt, sand, gravel. It also determines whether a given material is of relatively uniform gradation (all particles are of similar size) or whether it is well-graded (a wide range of particle sizes). For naturally occurring soils, the particle size distribution governs such properties as hydraulic conductivity, compacted density, shear strength, consolidation, workability and frost susceptibility.

Specific Gravity The specific gravity of a solid may be defined as the ratio of the weight in air of a given volume of solids at a given temperature, to the weight in air of an equal volume of distilled water at a given temperature. Because of the potential reaction of water with CaO in the ash, de-aired kerosene was used as a suspending fluid instead of distilled water, in accordance with Note 3 of ASTM D854-83 (2), with an appropriate correction applied to account for the difference in relative density between distilled water and kerosene. The samples, contained in 100 mL volume flasks, were kept under vacuum for 24 hr. Each sample was tested in an as-received condition. The specific gravity of the blended sample was 3.02.

Specific gravity is used in determining volume-weight relationships of a soil and is useful in estimating the disposal area volume for the wastes.



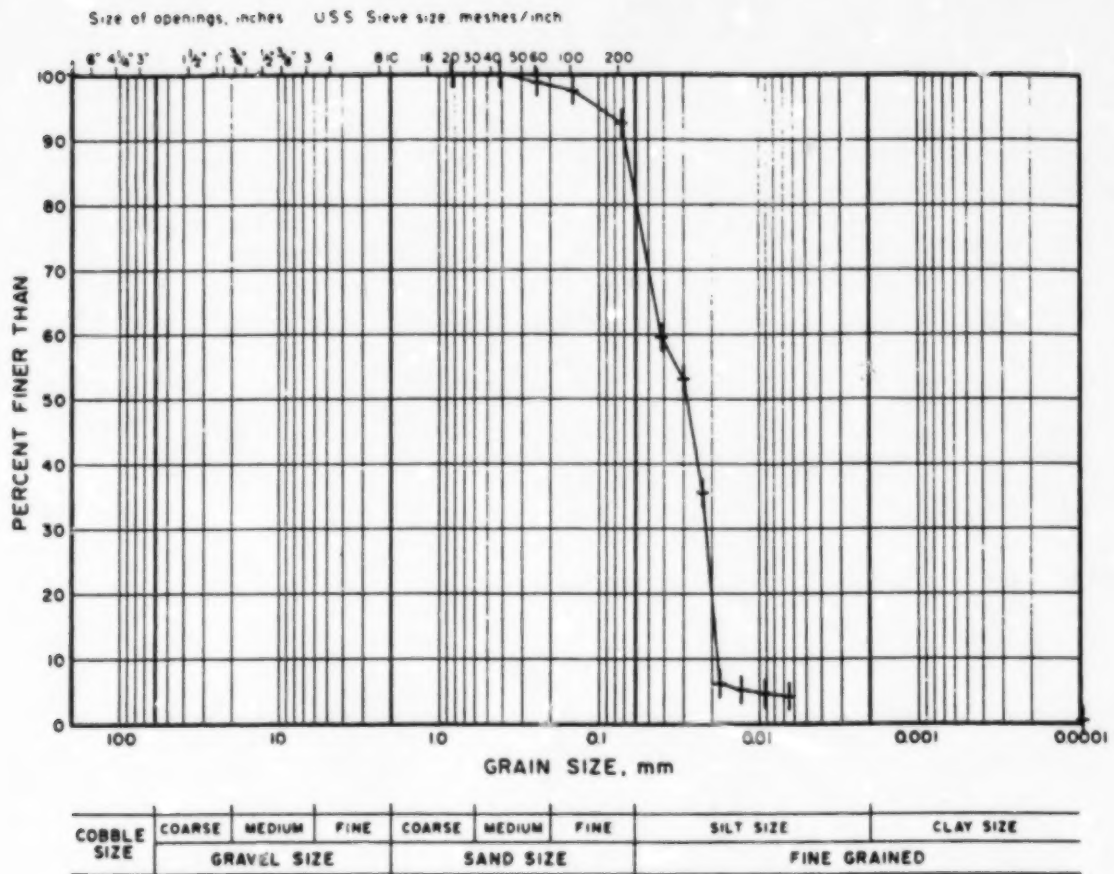


FIGURE 3: GRAIN SIZE DISTRIBUTION USING SIEVE AND HYDROMETER ANALYSIS

Standard Proctor This laboratory test provides the relationship between the dry density and the water content of a soil for a given compactive effort. ASTM method D698-78 (2) was used for this testing. The soil/water mixture is compacted into a standard 101.6 mm (4 in) diameter mould in 3 layers with 25 blows of a 2.49 kg (5.5 lb) hammer dropping 305 mm (12 in) on each layer. As the water content is increased, the density increases to a maximum value. Beyond this point, the density decreases, as the water content is further increased, while still applying the same compactive effort. The plot of dry density vs. water content defines the "maximum dry density" and the "optimum water content". It must be pointed out that the maximum dry density determined is for the compactive effort applied only; higher densities could be achieved in the field with heavy compaction equipment. The optimum water content is that water content which coincides with the maximum unit weight.

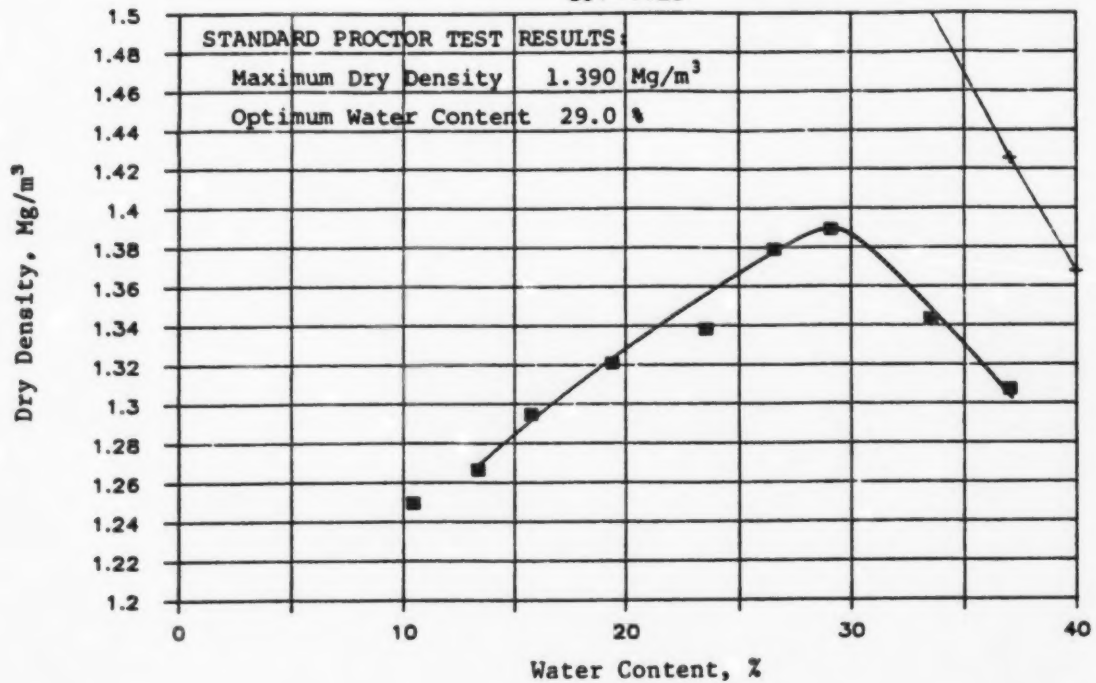
The maximum dry density determined in a laboratory compaction test serves as a standard for comparison with densities determined in the field during compaction of fill materials. The in-situ water content of the fill is compared with the optimum water content determined in the laboratory. In general, the in-situ water content should be within $\pm 2-3\%$ of the optimum water content to achieve satisfactory compaction in the field.

A Standard Proctor test was carried out on the blended sample, in which the sample was prepared for testing in two stages. Initially a water content of 15% was added to the sample. This was done to hydrate the CaO which was expected to present in the residue. The ensuing heat build-up, up to approximately 85°C, was allowed to cool over two hours, then the Standard Proctor test proceeded. The results of the Standard Proctor test are shown on Figure 4. The maximum dry density was 1.39 Mg/m^3 at an optimum water content of 29%.

Unconfined Compressive Strengths The unconfined compressive strength test consists of the application of an axial load to an unconfined cylindrical specimen of soil to determine the load per unit area at which the specimen will fail. Measurements of the applied stress and the axial strain are made to define the unconfined compressive strength at failure. ASTM method D2166-66 (2) was followed for this testing.

LABORATORY COMPACTION TEST

891-1125



+ 100% Saturation Line Gs 3.02 measured

FIGURE 4: STANDARD PROCTOR COMPACTION CURVE

Sample for the unconfined compression testing were compacted and cured in the same way as those samples prepared for the hydraulic conductivity tests. Upon compaction, the samples were extruded and trimmed to a nominal 50 mm x 100 mm cylinder.

Sample material was hydrated by the addition of 15% water to hydrate any CaO which was expected to be present. The samples were allowed to stand for two hours to allow the hydration reaction to occur and to allow the heat to dissipate. The samples were re-wetted to approximately 23% water content.

For the samples prepared for unconfined compressive strength, the material was compacted into Standard Proctor moulds at 100% compactive effort, trimmed, wrapped in Saran wrap and cured at 23°C for the required curing periods of 0, 8 and 12 days before testing. The only water available to the sample was that added during moulding.

Samples for freeze-thaw testing were prepared in the same way, extruded and trimmed to a nominal 50 mm x 100 mm cylinders. During curing, the samples were placed in a curing rack on wetted filter paper with the upper surface of the samples covered with plastic sheeting. Thus, the only source of water was from contact with the surrounding humid air or by capillary action through the filter paper.

The curing was carried out in a concrete curing room where the temperature and humidity were automatically controlled ($23^{\circ}\text{C} \pm 2^{\circ}\text{C}$; 100% humidity). For freeze-thaw testing, the compacted samples were placed in a freezer compartment for 23 hours then there were transferred into the curing room for 24 hours. This cycle was repeated for the required number of times. Table 3 presents the results of unconfined compressive strength testing.

Hydraulic Conductivity The objective of hydraulic conductivity testing is to determine the rate of discharge of water through a unit cross-sectional area of a porous medium (soil) under a unit hydraulic gradient and at standard temperature conditions. ASTM method D2434-68 (2) was followed for this testing. The results of this testing provide an indication of the potential of the waste to generate leachate. The samples were prepared and cured in the same manner as for the compressive strengths. Table 4 presents the results of this testing.

TABLE 3
SUMMARY OF UNCONFINED COMPRESSIVE STRENGTH TESTING OF
LABORATORY COMPATED SAMPLES ON BLENDED MATERIAL

Curing Condition	Water Content (%)		Dry Density (Mg/m^3)		Compressive Strength (kPa)
	Moulding	Final	Start	End	
0 Day	25.3	24.4	1.202	1.194	176
8 Days	23.6	23.3	1.305	1.302	1390
12 Days	20.5	18.1	1.320	1.293	4100
4 Cycle Freeze-Thaw	22.3	50.0	1.290	1.582	980
6 Cycle Freeze-Thaw	17.8	37.7	1.337	1.562	1550

Note: "End" dry density was determined after the curing or freeze-thaw cycling, but before the unconfined compressive strength test.

TABLE 4 SUMMARY OF CONSTANT HEAD HYDRAULIC CONDUCTIVITY TESTING OF
LABORATORY COMPACTED SAMPLES ON BLENDED MATERIAL

Curing Condition	Water Content (%)		Dry Density (Mg/m^3)		Coefficient of Permeability (k) cm/s
	Initial	Final	Start	End	
0 Day	21.4	35.5	1.283	1.283	1.47×10^{-5}
8 Days	24.8	34.5	1.294	1.329	8.10×10^{-6}
12 Days	25.9	39.0	1.392	1.106	5.51×10^{-6}
4 Cycle Freeze-Thaw	27.2	50.5	1.255	1.118	2.20×10^{-4}
6 Cycle Freeze-Thaw	26.1	34.0	1.255	1.232	1.28×10^{-4}

- Notes:
1. "Final" water content was determined after the permeability test was completed.
 2. "End" dry density was determined after the curing or freeze-thaw cycling, but before the permeability test.

3 CHEMICAL CHARACTERIZATION

The three samples; baghouse capture, bed drain and secondary cyclone return were separately chemically characterized to determine their major, minor and crystalline chemical constituents. The detailed methods used for these analyses are reported in reference 3. Table 5 summarizes the methods of analysis and the range of detection limits.

TABLE 5 SUMMARY OF ANALYTICAL METHODS

Components Determined	Methods	Detection limit
Total sulphur	Wet chemistry and Leco furnace with infrared detector	0.1%
Soluble sulfates	Wet chemistry	0.1%
Main components	X-ray fluorescence	0.01%
Trace components	X-ray fluorescence	10 ppm
Calcium sulfide	Wet chemistry	0.1%
Free calcium oxide	Wet chemistry	0.1%
Crystalline compounds	X-ray diffraction	
Total carbon	Leco furnace and infrared detection as CO ₂	0.1%
	Combustion and Coulometry	0.1%
Carbon as CO ₃ ²⁻ (from CO ₃ ⁼)	Wet chemistry and Coulometry	0.1% 0.1%
Loss on ignition (LOI)	950°C for 1 hour	-

X-ray fluorescence was used to quantify the main components of the three residues. These results are given on Table 6. Table 7 presents the results of the trace component analysis using this method. Table 8 presents the results of the analyses of the sample for sulphur species.

TABLE 6 ANALYSIS BY X-RAY FLUORESCENCE - MAIN COMPONENTS
For summation, elements are expressed as oxide percent of sample.
LOI = loss on ignition

Sample	SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	Fe ₂ O ₃	MnO	TiO ₂	P ₂ O ₅	LOI	Sum
Baghouse	10.9	3.66	49.6	1.06	0.14	0.19	11.5	0.10	0.17	0.40	4.31	82.0
Bed Drain	33.5	2.28	15.3	32.3	0.16	0.18	8.56	0.14	0.11	0.17	-0.15	92.6
Sec.Cyclone	10.5	2.34	53.8	2.26	0.11	0.21	8.04	0.10	0.12	0.25	1.31	79.0

TABLE 7 TRACE COMPONENTS
Results expressed as mg/kg as the element.

Sample	Cr	Rb	Sr	Y	Zr	Nb	Ba
Baghouse	<10	12	146	17	<10	<10	132
Bed Drain	2930	11	69	<10	26	<10	106
Sec. Cyclone	70	16	149	<10	21	12	91

TABLE 8 - ANALYSIS OF TOTAL SULPHUR, SOLUBLE SULPHATES AND SULPHIDES BY WET CHEMISTRY

Results expressed as % of sample.

Sample	Total Sulphur as sulphur	Soluble Sulphate as sulfur	Sulfide	Soluble sulphate as CaSO ₄
Baghouse	7.41	7.07	-	30.06
Bed Drain	2.97	2.33	-	9.92
Sec. Cyclone	8.87	8.67	-	36.86

Total sulfur was determined by wet chemistry and confirmed by Leco furnace with infrared detector. The results were consistent and only the average values are given here.

The results for total sulfur and soluble sulfate, obtained by different methods, are practically coincident, indicating that all the sulfur is present as soluble sulphate.

Sulphides are absent.

The three samples were also analyzed to determine their carbon dioxide and total carbon composition. The results are shown on Table 9.

TABLE 9 ANALYSIS OF CARBON DIOXIDE AND TOTAL CARBON
Results are given as % of sample expressed as indicated.

Sample	CO ²⁻	CO ²⁻ as CaCO ₃	CO ²⁻ as C	Total Carbon as C
Baghouse	2.06	4.69	0.56	2.90
Bed Drain	0.21	0.48	0.057	0.25
Sec. Cyclone	1.29	2.94	0.35	1.15

The total carbon was determined using a LECO analyzer with infrared detector following ASTM E 1019-87a (2). Total carbon was determined in order to verify the loss on ignition results. The CO₂ resulting from carbonates degradation is useful in calculating mass balances of compounds. In the past, some samples of FBC waste have contained up to 10% CaCO₃.

A principal task of the chemical characterization was to determine the crystalline composition of the three residues. A Philips PW 1710 diffractometer with cobalt excitation was used for the analyses. The diffractograms are presented in the appendix. Table 10 presents the major, minor and trace components of the samples.

The high percentage of MgO (32.3%) found in the Bed Drain sample by X-Ray Fluorescence, is in the form of Mg₂SiO₄, as indicated by the X-Ray diffractogram.

TABLE 10

RESULTS OF XRD ANALYSIS

Sample	Major Components	Minor Components	Trace Components
Baghouse	CaO	SiO ₂	
	CaSO ₄	Fe ₂ O ₃	
Bed Drain	CaSO ₄	SiO ₂	
	Mg ₂ SiO ₄	CaO	
Sec. Cyclone	CaO	SiO ₂	Fe ₂ O ₃
	CaSO ₄		Mg ₂ SiO ₄

Titration of the baghouse and secondary cyclone samples were performed to assist in the quantification of the CaO content of the residues. The results given below on Table 11. The titration of the bed drain was not performed due to high concentration of Mg₂SiO₄.

TABLE 11

TITRATION OF CaO

Results are given as % of sample, expressed as indicated.

Sample	Titration CaO	Obtained by difference CaO
Baghouse	34.5	34.6
Bed Drain	-	10.9
Sec. Cyclone	36.2	36.9

The results from the x-ray diffraction, x-ray fluorescence, sulphur species analysis and titrations have been combined to provide probable compositions of the three types of residues. These results are given on Table 12.

TABLE 12 - ESTIMATED COMPOSITION OF THE SAMPLES IN TERMS OF CHEMICAL COMPOUNDS
Figures represent % of compound.

Sample	CaSO ₄	CaCO ₃	CaO	Mg ₂ SiO ₄	Fe ₂ O ₃	Others	LOI corr.	Sum
Baghouse	30.1	4.7	34.6	-	11.5	16.6	2.3	99.8
Bed Drain Sec.	9.9	0.5	10.9	56.4	8.6	12.5	-	98.8
Cyclone	36.9	2.9	36.9	3.9	8.0	11.9	0.02	100.5

All the sulphate were determined by wet chemistry and calculated as CaSO₄. The CaO was calculated by difference;

$$\begin{aligned} \text{CaO\%} &= \text{Total Ca (as CaO\%)} - \frac{\text{CaO}}{\text{CaSO}_4} \times \text{CaSO}_4\% - \frac{\text{CaO}}{\text{CaCO}_3} \times \text{CaCO}_3\% \\ &= \text{Total Ca (as CaO\%)} - 0.412 \times \text{CaSO}_4\% - 0.560 \times \text{CaCO}_3\% \end{aligned}$$

The titrations of the first and third samples confirm these calculations by difference. According to the results of X-ray diffraction, the magnesium component of the bed drain and secondary cyclone samples has been assumed to be entirely as Mg₂SiO₄. The main contributor of the column "others" in SiO₂ with less amounts of the components given in Table 5.

LOI_{corr} is the loss on ignition (LOI), from which the CO₂ from CaCO₃ has been deducted, as its mass is already taken into account in its parent compound.

The sum of all the columns gives results close to 100%, indicating internal consistency in the estimates of the table.

4 SULPHUR SPECIFICATIONS

Most of the sulphur captured by the limestone in AFB combustors is present in the discharged residues as anhydrous calcium sulphate (CaSO_4) (4-7). However, accumulations of sulphide have been reported in residues from some small- and pilot-scale circulating fluidized-bed combustors (8-10). The presence of significant amounts of sulphide in residues from full-scale, utility FBC system would present considerable problems with respect to their utilization or disposal. The data are to be compared with the findings from an earlier study (10) during which significant sulphide levels were detected in some sample materials from the same source.

Figure 1 shows a schematic drawing of the circulating combustor and its associated flue-gas cleaning systems, with indications of the seven locations from which samples were withdrawn. Because the CFBC-solids are potentially sensitive to both oxidation and hydration when exposed to the atmosphere, sampling methods were developed that permitted collection of solids from the operating combustor under a dry N_2 atmosphere. The devices used to obtain samples from the combustor during operation have been described elsewhere (10). Because it is exposed to air during normal operations, material from the baghouse (point 7) was collected without protection by nitrogen. All samples used in the study were withdrawn on December 11, 1988, starting at 02:30 (termed sampling event C2). The samples form a second series comparable with a set obtained on March 7, 1988 (termed sampling event C1). The samples have been labeled C1-1, through C1-7 for the first series (March 7, 1988), and C2-1 through C2-7 for the second series (December 11, 1988). Details of a more extensive study on the C1-series samples are to be given in a report under preparation (10).

To obtain materials for laboratory examination, samples C2-1 through C2-6 were individually blended, riffled and subsampled under dry N_2 in a glove box. Samples from point 7 were handled in the laboratory atmosphere. The same procedure had been followed for the C1-series materials.

Chemical analyses for major and minor elements were performed using ICAP methods. A standard technique originally devised for analysis of blast furnace slags (AOAC method) (11) was used to determine sulphide in the solids and thermogravimetry (TGA/DTG) was used to investigate phase composition. X-ray diffraction (XRD) was used to examine Sample C2-7 (Figure 5).

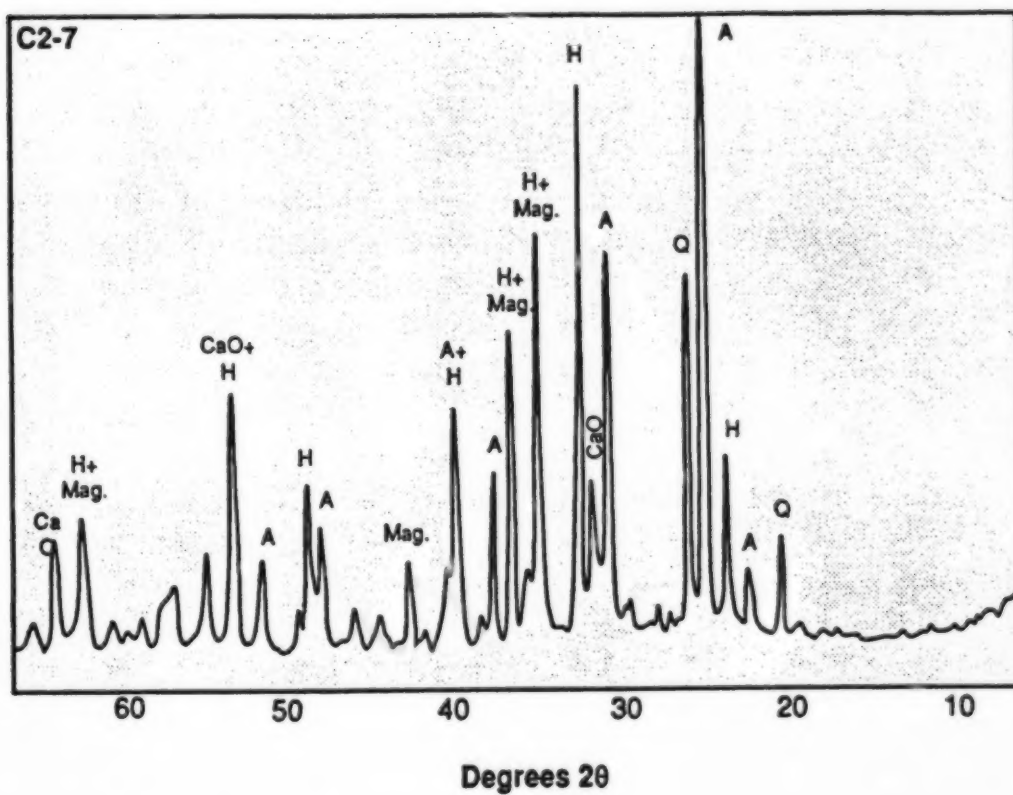


FIGURE 5: X-RAY DIFFRACTION PATTERNS(CuK) FOR SAMPLE C2-7 RECOVERED FROM THE CFB COMBUSTOR SHOWING IDENTIFICATION OF PHASES: Q, QUARTZ H, HEMATITE, MAG, MAGNETITE, A, ANHYDRITE, CaO, CALCIUM OXIDE.

4.1 Chemical Characteristics

Chemical compositions of the seven samples (C2-1 through C2-7) are given in Table 13 reported as major oxides, total carbon, total sulphur and sulphide (as S^{2-}). From the chemical analyses, it is clear that the samples may be categorized into two general groups as follows:

1. Samples C2-1 through C2-5, these being the materials from the circulating particulate load, are of generally similar composition without regard to the sampling location. Chemically, the circulating solids may be considered as a single sample type with SiO_2 , 20 to 24%; CaO , 28 to 33%; and LOI , 1.3 to 1.5%. Total carbon was in the range from 0.2 to 0.5%. Samples C2-1 through C2-5 also contained substantial quantities of magnesium (13.5 to 18.5% as MgO) presumed to have originated from the olivine start-up bed. Sulphur in the circulating solids was in the range 7.4 to 8.8% as total sulphur, with minimal sulphide (0.2 to 0.3%).
2. Samples C2-6 and C2-7, from the secondary cyclone and the baghouse respectively, showed different characteristics. In comparison with the circulating solids, silicon content was lower (15 - 17%, as SiO_2), and the materials exhibited higher loss-on-ignition (2.16 and 7.28 respectively). These samples were distinguished from the circulating materials by the presence of higher levels of total carbon (1.28 and 5.32% respectively). Total sulphur in samples C2-6 and C2-7 was 9.6% and 8.1% respectively, with minor sulphide content (0.44 and 0.30% respectively).

Although the differences between the two sample groups are clear, they are not as distinct as those found between the circulating solids and baghouse capture among the C1-series materials (Table 14). In those samples the most notable differences were relatively high levels of high sulphide and carbon in the secondary cyclone and baghouse solids.

TABLE 13 - CHEMICAL ANALYSIS (MASS %) OF FBC RESIDUES (C2- SERIES)

Element Oxide	C2-1	C2-2	C2-3	C2-4	C2-5	C2-6	C2-7
SiO ₂	21.35	20.02	24.14	21.01	20.33	15.48	17.02
Al ₂ O ₃	3.49	3.22	2.70	3.43	3.01	4.41	7.01
Fe ₂ O ₃	6.94	6.84	7.94	7.22	6.42	12.00	21.96
CaO	31.68	32.91	28.56	31.83	32.39	39.36	25.97
MgO	13.62	13.74	18.47	13.67	14.02	1.22	0.48
Na ₂ O	0.17	0.12	0.13	0.13	0.12	0.14	0.18
K ₂ O	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.48
LOI	1.30	1.38	1.43	1.50	1.39	2.16	7.28
Sulphur	8.03	8.77	7.36	8.11	8.64	9.64	8.11
Sulphide	0.30	0.27	0.20	0.23	0.20	0.44	0.30
Carbon	0.20	0.38	0.14	0.49	0.35	1.48	5.32

TABLE 14 - CHEMICAL ANALYSIS (MASS %) OF FBC RESIDUES (C1-SERIES)

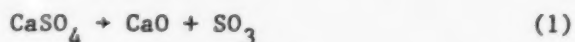
Element Oxide	C1-1	C1-2	C1-3	C1-4	C1-5	C1-6	C1-7
SiO ₂	28.89	29.50	26.40	28.10	29.99	12.99	10.89
Al ₂ O ₃	5.19	5.20	4.81	4.79	4.29	3.12	3.66
Fe ₂ O ₃	9.58	9.20	9.05	9.21	9.18	8.48	10.56
CaO	27.78	27.95	28.07	29.07	26.16	48.97	50.09
MgO	14.76	15.60	13.88	15.08	19.97	3.80	0.71
Na ₂ O	0.27	0.21	0.20	0.21	0.20	0.19	0.18
K ₂ O	0.43	0.14	0.15	<0.10	0.10	<0.10	<0.10
LOI	0.15	0.41	0.15	-0.23	-0.19	7.52	7.99
Sulphur	6.15	6.19	6.41	6.38	5.49	8.27	8.82
Sulphide	0.50	0.50	0.60	0.50	0.50	2.60	2.30
Carbon	0.83	1.13	0.71	1.64	0.64	9.23	10.00

Thermogravimetric analyses was conducted on samples C2-1 through C2-7 (Figure 6). For each sample three regions of mass loss were examined. Minor mass losses were observed (Table 15) over the ranges 350 to 500°C, and 500 to 750°C attributed to the presence of minor quantities of Ca(OH)_2 and CaCO_3 respectively. An extensive mass loss occurred at temperatures in excess of 750°C and was not complete at 1000°C (the maximum temperature to which the TGA equipment could be raised).

TABLE 15 - THERMOGRAVIMETRIC MASS LOSS (%) FROM FBC RESIDUES (C2-SERIES)

Temperature Range (°C)	C2-1	C2-2	C2-3	C2-4	C2-5	C2-6	C2-7
400 - 500	0.02	0.13	0.06	0.17	0.12	0.02	0.09
500 - 750	0.05	0.33	0.16	0.45	0.29	0.47	0.85
750 - 1000	(-0.01)	0.29	0.13	0.82	0.31	12.06	25.15

At the present time, the origin of the mass loss above 750°C, has not been established. It is possible that it resulted from the decomposition of calcium sulphate:



This reaction is known to occur for pure CaSO_4 at temperatures over 1200°C, but it may be sufficiently accelerated by the presence of a number of compounds (including silicates and carbon) to proceed almost to completion in the TGA experiment at lower temperatures (12-17). Alternatively, the mass loss may have resulted from the reduction of CaSO_4 . The reactions involved in this process are relevant to the potential formation of CaS and are discussed in a subsequent section of this report.

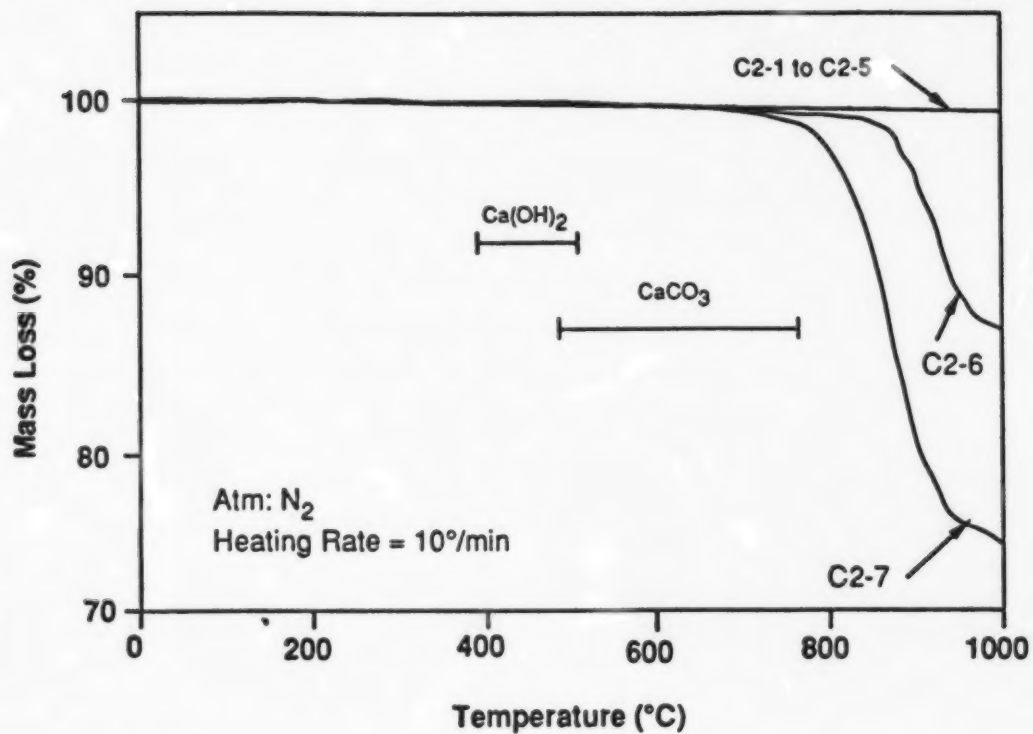


FIGURE 6: THERMOGRAVIMETRIC ANALYSIS CURVES FROM CFBC RESIDUES SHOWING MASS LOSS ABOVE 750°C .

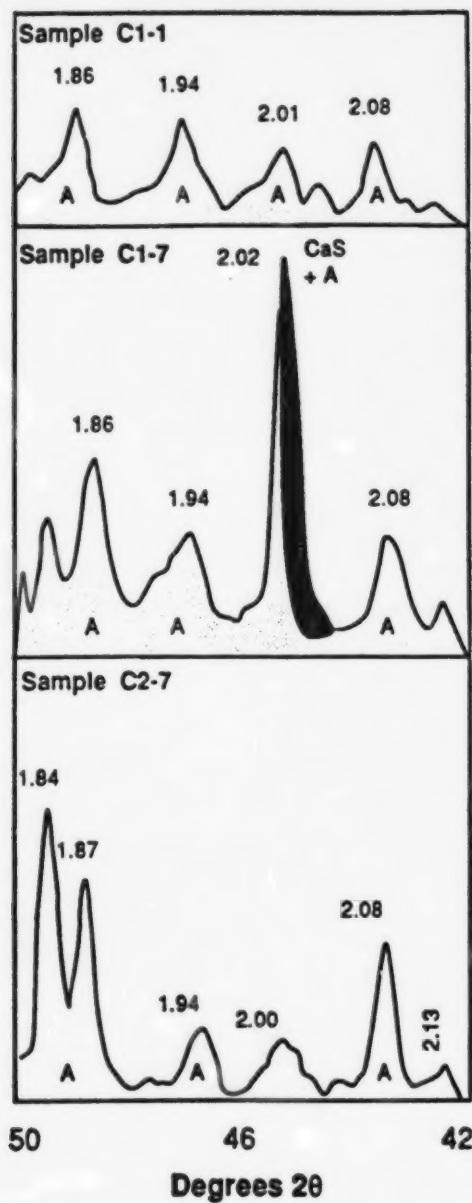


FIGURE 7: DETAILS OF THE XRD PATTERNS FOR SAMPLES C1-1, C1-7 AND C2-7 IN THE 2.00 Å REGION SHOWING THE OVERLAP OF DIFFRACTION LINES DUE TO ANHYDRITE (A) AND CALCIUM SULPHIDE (CaS).

4.2 Phase Composition

Chemical analysis showed the solids to be largely sulphated calcined limestone, olivine and quartz. Only minor quantities of sulphide (0.20 to 0.44%) were found in the C2-series materials. Table 16 summarizes calculated values for the phase composition of Samples C2-1 through C2-7 in terms of carbon, CaO, Ca(OH)_2 , CaCO_3 , CaSO_4 and CaS contents. For comparison, a similar summary is given in Table 17 for the phase composition of the C1-series solids. These calculations are based on the data from chemical analysis and TGA. In making these calculations it has been assumed that the small quantities of sulphide detected were present as CaS in the samples. This may not be the case, especially in the presence of substantial quantities of iron in various valence and combination states.

In comparison with the samples from the C1-series the most marked feature is the low level of sulphide in all the C2-series samples. Sulphide in the C1-6 and C1-7 samples was attributed (9) to the presence of CaS on the basis of the overall composition of the solids. Based on this, it was considered reasonable to anticipate that much of the sulphide may be present as CaS. XRD data in the $2.00 \text{ \AA}$ region (Figure 7, were used to confirm that both of the C1-6 (baghouse) and C1-7 (secondary cyclone) solids contained crystalline CaS in addition to anhydrite (CaSO_4), the latter being the predominant sulphur-containing phase. No evidence for other sulphide containing phases was found. The low level of sulphide present in the C2-7 series samples precluded identification by XRD (Figure 7).

4.3 Sulphur Speciation and the Mechanism of Formation of CaS

The chemical analysis clearly showed that sulphur captured from the combustion gases was present in all of both the C1- and C2-series samples, regardless of their point of collection from the combustion system. The solids forming the circulating mass (Samples C2-1 to C2-5) contained total sulphur levels in the range 7.4-8.8% S. The materials removed from the combustion gases by the secondary cyclone and the baghouse contained more sulphur in total (9.6 and 8.1% S, respectively).

TABLE 16 - CALCULATED PHASE COMPOSITION OF FBC RESIDUES (C2-SERIES)

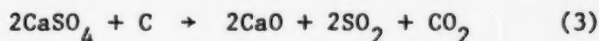
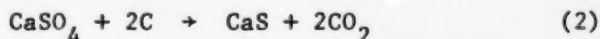
Element Oxide	C2-1	C2-2	C2-3	C2-4	C2-5	C2-6	C2-7
CaS	0.68	0.61	0.45	0.52	0.45	0.99	0.68
CaSO ₄	32.85	36.13	30.43	33.49	35.87	39.10	33.19
CaCO ₃	0.11	0.75	0.36	1.02	0.66	1.07	1.93
Ca(OH) ₂	0.08	0.53	0.25	0.70	0.49	0.08	0.37
CaO	17.50	16.74	15.28	16.53	16.52	21.82	10.41
Carbon	0.19	0.29	0.10	0.37	0.27	1.35	5.09

TABLE 17 - CALCULATED PHASE COMPOSITION OF FBC RESIDUES (C1-SERIES)

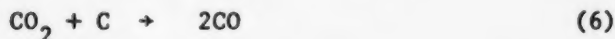
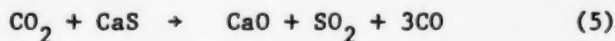
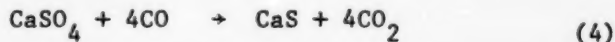
Element Oxide	C1-1	C1-2	C1-3	C1-4	C1-5	C1-6	C1-7
CaS	1.13	1.13	1.35	1.13	1.13	5.85	5.18
CaSO ₄	24.01	24.18	24.69	24.99	21.21	24.10	27.71
CaCO ₃		0.18				13.03	6.74
Ca(OH) ₂		0.74				4.85	5.47
CaO		16.45				25.45	23.36
Carbon		1.11				7.67	9.19

The oxidation state of sulphur was not found to be dependent on the location of the solids in the system for the C2-series solids all of which showed sulphide contents in the range 0.20-0.44% S^{2-} by mass. This is in marked contrast to the solids from the C1-series where sample C1-6 and C1-7 showed sulphide levels of 2.6 and 2.3% respectively together with substantial carbon content.

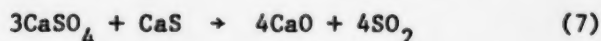
The presence of CaS in the C1-series of samples was attributed to reduction of $CaSO_4$ through a complex sequence of reactions involving C, CO and CO_2 brought about by reducing or low-oxidation conditions in the gas collection system during combustion. Turkdogan and Vinters (18) have examined the reduction of $CaSO_4$ by carbon in some detail under conditions where either CaS or SO_2 is the principal product of reduction. The following reactions were proposed:



Because these solid-solid reactions are inherently slow, the reduction of $CaSO_4$ to CaS or SO_2 is expected (18) to proceed via the intermediate reaction products, CO and CO_2 :



Experimentally, Turkdogan and Vinters (18) found that SO_2 evolution and loss of CaS continued in systems with low carbon content even after all of the carbon had been consumed. This lead them to propose a further competing solid-solid reaction:



The overall reaction process was shown by Turkdogan and Vinters (18) to preferentially produce either CaS or SO_2 depending on the amount of carbon present and its reactivity. In mixtures where the ratio of carbon to sulphur (C:S) was approximately 0.5, complete conversion to SO_2 was attained. Where C:S was slightly above the stoichiometric value (=2) for reaction (3), conversion to CaS was attained with less than 1% loss as SO_2 . It is probable that these reactions are also responsible for the mass losses at temperatures over 750°C in the TGA experiments.

If reduction of CaSO_4 is the means whereby CaS was produced in the CFB combustor, during the Cl-series experiments, it remains to be considered where in the system the reaction occurs. The chemical analyses of the solids from the Cl-series showed that sulphide and carbon both accumulated with spent limestone particles in the secondary cyclone and the baghouse. The major part of the combustor, the loop containing the circulating solids, is largely under oxidizing conditions maintained by the primary (fluidizing) air and the introduction of secondary air below the L-valve (Figure 1). It is unlikely that CaS would form by reduction in these regions of the system, as is consistent with the observed low sulphide-content of Samples C-1 to C-5.

The baghouse operates at a gas temperature of 80-120°C. Thus, despite the availability of carbon, and the consequent potential for reduction, it is not considered likely that CaSO_4 reduction could take place in the baghouse catch. The secondary cyclone operates at a gas temperature close to 850°C, at which temperature according to reaction (2), $\Delta G^\circ = -53,438 \text{ cal/mole}$ (17). In the Cl-series, the ratio C:S in the discharged solid (Sample Cl-6) was 2.98, well in excess of the minimum stoichiometric requirement for reduction to CaS to predominate. It must be concluded that the potential existed under these conditions for reduction of CaSO_4 by carbon to form CaS in the secondary cyclone. Its presence in the baghouse discharge (Cl-7) is assumed to have been a consequence of carry-over of fine particles from the secondary cyclone.

It is suggested that the combustion conditions when the C2-series of samples were collected were such that carbon had not accumulated in the secondary cyclone. It should be noted that the C:S ratio of the secondary solids (C2-6) is 0.41 compared with 2.98 for the Cl-6 material. This situation would be consistent with formation of CaS in the Cl-series but not in the C2-series solids, any reduction of CaSO_4 under these conditions would have proceeded to produce SO_2 .

4.4 Summary

The following comments as to the nature of sulphur capture in CFBC residues can be drawn from the present study in comparison with the previous work:

- It is clear that whereas sulphur is captured and retained in solid phases throughout the circulating bed, its state of combination can be altered by secondary reactions.
- Consistent with previously reported work, the bulk of the captured sulphur in the bed materials is present as CaSO_4 , intimately mixed with CaO from calcined limestone.
- Circumstances can exist in the combustor whereby reduced sulphur species are formed, or captured. Among these, sulphides have been identified that appear to be present largely as calcium sulphide.
- Calcium sulphide when found is predominantly present in solids collected from the gas cleaning and cooling system. Its presence appears to be associated with the availability of carbon in regions where reduction conditions may prevail. At present, indications are that it is formed at about 850°C in the secondary cyclone, by reduction of CaSO_4 through a complex sequence of reactions involving C, CO and CO_2 . When the carbon content of the solids in the secondary cyclone does not reach levels at which the C:S ratio exceeds approximately 2.0, it appears that CaS formation is not favoured. It has been reported that during the C-1 trial considerable solids holdup was experienced in the combustor. These conditions are consistent with the chemical conditions favouring CaS formation.
- Because the limestone used in the C2-series experiments differed from that used in the C1-series, it is possible that the nature of the limestone bed plays some role in sulphur capture and oxidation state. It is recommended that this be investigated by examination of samples taken using the

Elmtree/Textlime combination under conditions of combustion similar to those prevailing during the C2-series experiment.

- The mass loss at high temperature in the thermogravimetric analysis experiment appears likely to result from the same reaction sequence that produces CaS of SO_2 by reduction of CaSO_4 . It is recommended that these reaction be investigated further to elucidate the processes that are probably occurring in the secondary cyclone solids during combustion.

5 DISCUSSION

One objective of this investigation was the development of characterization data on residue samples generated on the modified UBC pilot scale test rig. Comparisons could then be made between the residues produced before and after modifications to the pilot scale combustor and to wastes produced at the Chatham 22 MW_e CFBC unit. This section of the report presents these comparisons.

5.1 Comparison of Geotechnical Properties

Table 18 presents a comparison of the geotechnical properties of residues produced at the UBC pilot plant before and after modifications to the combustor and the characteristics of samples from the Chatham unit. The particle size distributions of the three materials were generally similar, however as shown on Figure 8, the modifications to the UBC unit caused a decrease in D₉₀ range from about 0.2 mm down to 0.075 mm. Thus, it can be seen that the modifications to the UBC pilot unit produced wastes of more uniform particle size distribution. In terms of specific gravity and standard Proctor tests, the modifications appear to produce residues more similar to these from Chatham.

Compressive strengths under all conditions tested were greater for the residues from the modified UBC pilot scale unit. For example, the strength after 8 days increased from about 300 to 1400 kPa. In comparison with Chatham residue, this strength was less than half that determined after 7 days of curing.

Hydraulic conductivities of the wastes from the modified UBC pilot plant were less than those of the residues produced before modifications were made. For the two cases where similar data are available, the post-modification and Chatham waste hydraulic conductivities were similar.

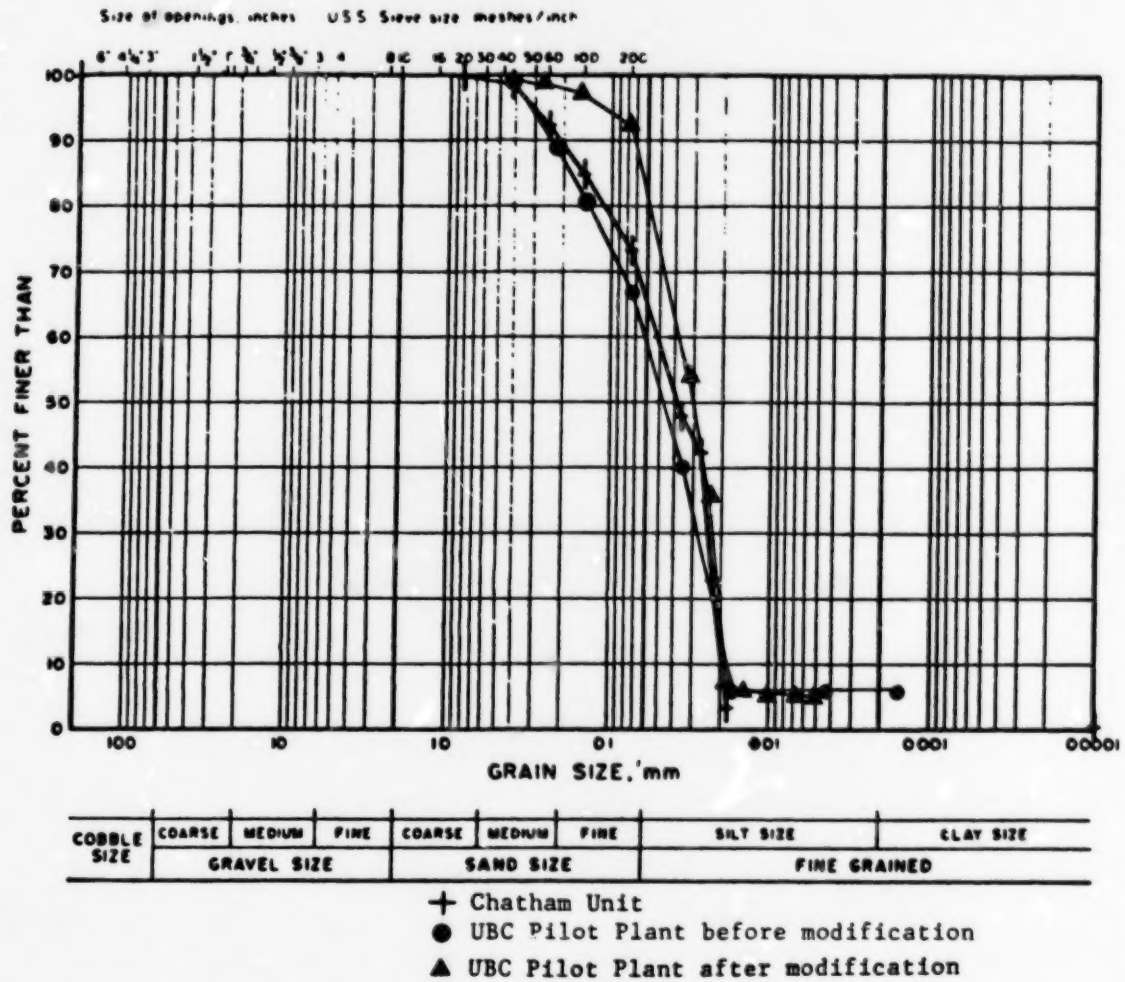


TABLE 18 COMPARISON OF GEOTECHNICAL PROPERTIES

UBC Pilot Plant			
Property	Before Modification + After Modification		Chatham Unit*
Particle Size Distribution (mm)			
D ₉₀	0.25	0.07	0.2
D ₅₀	0.04	0.03	0.035
D ₁₀	0.03	0.02	0.02
Specific Gravity	2.58	3.02	2.95
Standard Proctor			
Max dry density (Mg/m ³)	1.31	1.39	1.388
@ % water	32.4	29.0	26.5
Compressive Strength (kPa)			
after 0 days		176	-
after 8 days	309	1390	4120 (7 days)
after 12 days	461	4100	-
after 4 freeze thaw cycles	201	980	-
after 6 freeze thaw cycles	sample failed	1550	3200 (7 cycles)
Hydraulic Conductivity (cm/s)			
after 0 days	4.53 x 10 ⁻⁵	1.47 x 10 ⁻⁵	-
after 8 days	4.53 x 10 ⁻⁵	8.1 x 10 ⁻⁶	1.7 x 10 ⁻⁶ (7 days)
after 12 days	3.86 x 10 ⁻⁵	5.51 x 10 ⁻⁶	-
after 4 freeze thaw cycles	1.54 x 10 ⁻⁵	2.20 x 10 ⁻⁴	-
after 6 freeze thaw cycles	3.6 x 10 ⁻⁸	1.28 x 10 ⁻⁴	1.6 x 10 ⁻⁴ (7 cycles)

Note: + Data from Reference 19

* Data from Reference 20

Table 19 presents a comparison of the principal chemical composition of the same three wastes. Generally, the three chemical compositions were similar with the following exceptions. Both results from the UBC pilot plant has similar Fe₂O₃ concentrations of between 9 and 10 percent. This contrasts with the Chatham residue which had 15.9 %. The component consisting of others (mainly SiO₂) and Mg₂SiO₄ ranged from a low for residues from the Chatham Unit of 24.2% to 33.8% for the unmodified UBC pilot plant to 37.07% for the modified UBC pilot plant.

TABLE 19 COMPARISON OF CHEMICAL COMPOSITION

Compound	UBC Pilot Plant		Chatham Unit +
	Before Modification	After Modification*	
CaSO ₄	21.7	22.85	26.1
CaCO ₃	5.2	2.57	4.6
CaO	24.7	25.54	23.5
CaS	0.7	ND	0.45
Mg ₂ SiO ₄	-	22.57	-
Fe ₂ O ₃	9.1	10.0	15.9
Others	33.8	14.50	24.2
LOI	5.1	1.60	4.3
SUM	100.3	99.50	99.0

Note: + data from reference 21

* Average calculated on blend proportion

ND is not detected

The LOI was lowest for the modified UBC pilot plant (1.6%) which was about one third of the value reported in the waste before modifications. The former was less than half the value of the quantified in the Chatham residue.

Although very small but measurable concentrations of CaS were previously found in the UBC pilot plant residue and the Chatham waste, none was found in the UBC pilot plant after the modifications.

6 REFERENCES

1. Grace, J.R., and C.J. Lim, Circulating Fluidized bed Combustion of Coal, Woodwastes and Pitch, Final Report under Energy, Mines and Resources Canada, Contract 24St.23440-6-9007, December 1987.
2. ASTM, Annual Book of ASTM Standards, American Society for Testing and Materials, Philadelphia, PA, 1982.
3. Dearborn Environmental Consulting Services, Determination of the Calcium Oxide Content of Combustion Wastes, DSS File No: KE145-4-1062, DECS File No: W10-602, April 26, 1985.
4. McLaren, J. and D.F. Williams, J.Inst. Fuel: 303, August, 1969.
5. Minnick, J.L., Development of Potential Uses for the Residue from Fluidized Bed Combustion Processes, Reports under Contract No. EF-77-C-01-2549.
6. Minnick, J.L., Development of Potential Uses for the Residue from Fluidized Bed Combustion Processes, Reports under Contract No. DE-AC21-77-ET10415.
7. Collins, R.J., J. Testing and Evaluations (8): 259, 1980.
8. Dearborn Chemical Company, Characterization of Circulating AFBC Wastes, Canadian Electrical Association Report No. 432 G 494, December 1986.
9. Anthony, E.J., The Presence of Calcium Sulphide in Solid Wastes from Circulating Fluidized Bed Combustors, CANMET Division Report ERP/ERL 86-53 (TR), September 1986.
10. Berry, E.E., Hemmings, R.T., and B.J., Cornelius, ORTECH International Report; In progress.
11. AOAC Methods 13th Edn. Method 1.013-1.015, "Sulfide Sulfur (7)-Final Action," 1980.
12. Berry, E.E., J. Appl. Chem. Biotechnol (22): 673, 1972.
13. Hofmann, H.O. and W. Mostowitsch, Trans. Am Inst. Min. Metall. Engrs.(39): 628, 1908.
14. Bedwell, M.L., Rep. R. Inst. Chem (3): 1952.
15. Frydlander, J.H., Rev. Prod. Chem. (29): 613, 1926.
16. Higson, G.I., Chem Eng. News (29): 4469, 1951.
17. Manning, J., Proc. Fertil. Soc. (15): 1951.
18. Turkdogan, E.T., and J.V. Vinters, Trans. Inst. Mining and Met., Section C, 85 pp. C117-C123, 1976.

19. Dearborn Environmental consulting Services, Geotechnical Testing of CFBC Residues from the UBC Pilot Plant, DSS File No: SSKE 145-6-0643, DECS File NO: S10-607, March 31, 1988.
20. Anthony, E.J., Ross, G.G., Berry, E.E., Hemmings, R.T., Kissel, R.K. and C.C. Doiron, "Characterization of Solid Wastes from Circulating Fluidized Bed Combustors," Presented at 1989 International Conference on Fluidized Bed Combustion, San Francisco, April 30, 1989.
21. Dearborn Environmental Consulting Services, Technical Options for the Disposal of Circulating Fluidized Bed Combustion Solid Wastes, DSS File No: SS.KE 145-6-0643, DECG File No: S10-609, March 1989.

APPENDIX A

UNITED STATES GOVERNMENT PRINTING OFFICE: 1969

13720215:3

C-1

13720215:3	29-03-1969	15.03
5.000	20.3285	71
24.275	4.2571	54
26.627	3.8876	543
29.687	3.4940	123
31.035	3.3458	134
36.515	2.8571	203
37.632	2.7752	49
38.740	2.6988	505
43.709	2.4845	65
48.161	2.3311	48
50.911	2.0825	73
57.221	1.8692	53
61.464	1.7516	193
63.527	1.7004	41
65.794	1.6488	

73.000 1.4703
29-03-1969 15.28

SECONDARY
CYCLONE

map 6 070

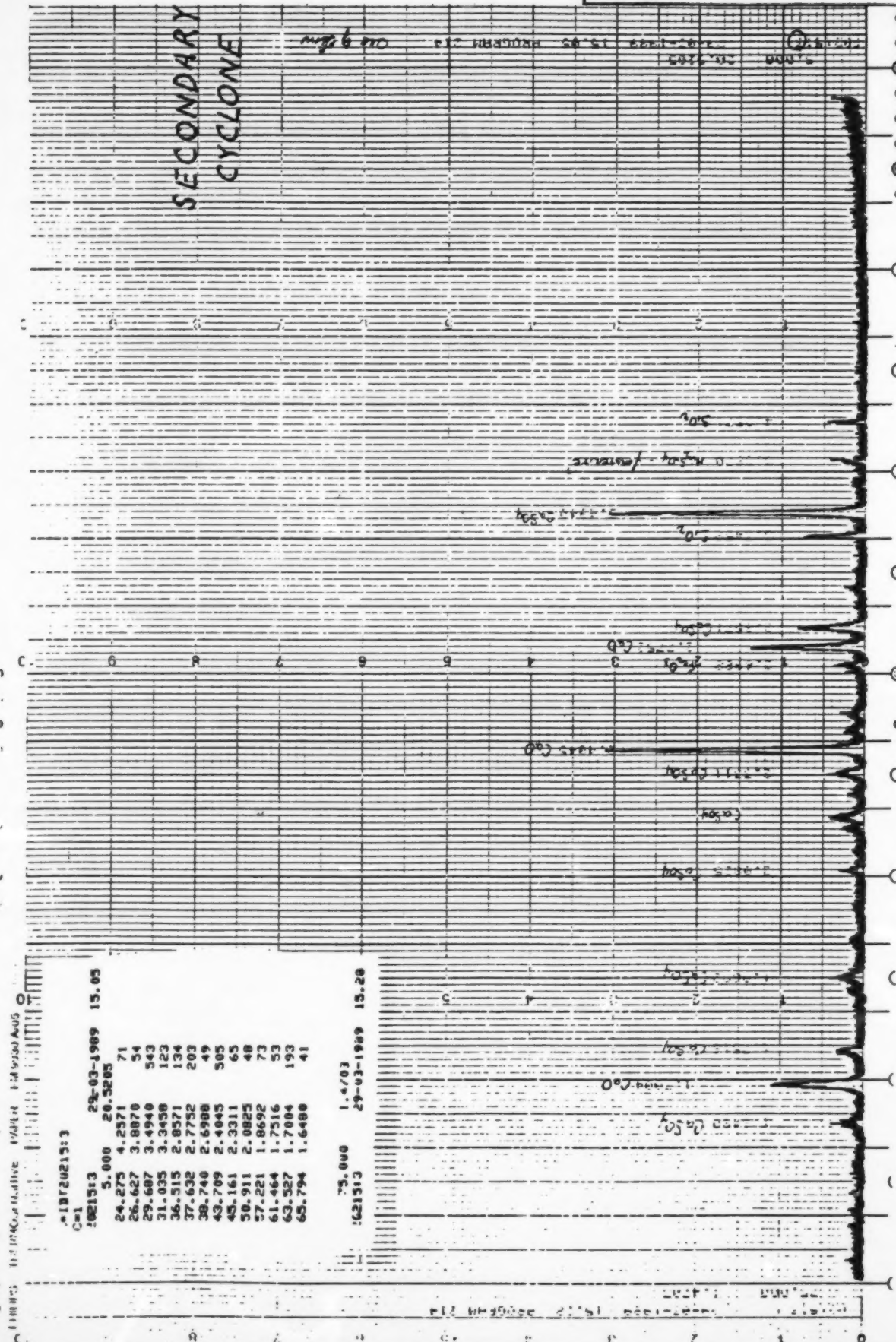
13720215:3

29-03-1969

15.03

15.03

13720215:3



PHILIPS THERMOSENSITIVE FILM 1200 10 A05

10-2021511

29-03-1969 10.30

24.238	5.000	20.3205	47
28.127	4.2600		52
29.599	3.6836		507
31.044	3.4926		171
36.554	3.3440		133
37.617	2.8542		220
38.743	2.7763		99
41.557	2.6986		75
43.717	2.5173		542
45.535	2.4041		53
47.774	2.3275		61
57.223	1.8692		70
63.522	1.7005		229
65.786	1.6482		48

75.000 1.4703

10-2021511 29-03-1969 10.02

BAGHOUSE

10-2021511

10-2021511 29-03-1969 10.02

10-2021511 29-03-1969 10.02

10-2021511 29-03-1969 10.02

10-2021511 29-03-1969 10.02

10-2021511 29-03-1969 10.02

10-2021511 29-03-1969 10.02

10-2021511 29-03-1969 10.02

10-2021511 29-03-1969 10.02

10-2021511 29-03-1969 10.02

10-2021511 29-03-1969 10.02

10-2021511 29-03-1969 10.02

10-2021511 29-03-1969 10.02

10-2021511 29-03-1969 10.02

10-2021511 29-03-1969 10.02

10-2021511 29-03-1969 10.02

10-2021511 29-03-1969 10.02

10-2021511 29-03-1969 10.02

Q. H. 7:6:702.01.